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United States Department of Commerce Technology Administration National Institute of Standards and Technology

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Flammability Studies of Polymer Layered Silicate (Clay) Nanocomposites

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Background

In the pursuit of improved approaches to fire retarding polymers a wide variety of concerns must be addressed, in addition to the flammability issues. First, the low cost of commodity polymers requires that the fire retardant (FR) approach also be of low cost. This limits one primarily to additive type approaches. Second, these additives must be easily processed with the polymer. Finally, any additive must not excessively degrade the other performance properties of the polymer, and must not create environmental problems in terms of recycling or disposal of the end product. Polymer layered silicate (PLS) nanocomposites are materials that may partially fulfill the above requirements for high performance flame retardant products.

PLS nanocomposites are hybrid organic polymer - inorganic materials with unique properties when compared to conventional filled polymers (1). For example, the mechanical properties of a nylon-6 layered-silicate nanocomposite, with a silicate mass fraction of only 5 %, show excellent improvement over those for the pure nylon-6. The nanocomposite exhibits a 40 % higher tensile strength, 68 % greater tensile modulus, 60 % higher flexural strength, and a 126 % increased flexural modulus. The heat distortion temperature (HDT) is increased from 65° C to 152° C (2). Some PLS nanocomposites exhibit increased thermal stability: an important property for improving flammability performance, as well as decreased gas permeability, and increased solvent resistance, along with the improved physical properties.

Methods to prepare PLS nanocomposites have been developed by several groups over the last few decade (3, 4, 5, 6, 7, 8, 9). In general these methods achieve molecular level incorporation of layered silicate (e.g., montmorillonite) into the polymer by addition of a modified silicate; during the polymerization (in situ), or to a solvent swollen polymer, or to the polymer melt (1). Two terms (intercalated and delaminated) are used to describe the two general classes of nano-morphology that can be prepared. The intercalated structure results when the extended polymer chains are inserted into the gallery space between the individual silicate layers. These are well ordered multi-layered structures. The delaminated (or exfoliated) structures result when the individual silicate layers are more completely dispersed in the organic polymer. The interlayer spacing (5 nm -200 nm) is on the order of the radius of gyration of the polymer. The silicate layers in a delaminated structure may have the same well ordered multi-layer structure as the intercalated morphology, or they may be significantly less ordered (10).

We have reported previously on the flammability properties of *delaminated* nylon-6 layered silicate nanocomposites and *intercalated* polymer layered-silicate nanocomposites prepared from polystyrene

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(PS) and polypropylene-graft-maleic anhydride (PP-g-MA) (11,12). Here, we will briefly review these results and report on our initial studies of the flame retardant mechanism.

We have characterized flammability properties of representative thermoplastic and thermoset polymer layered silicate nanocomposites. The peak and average heat release rates (HRR) are reduced by 40 % to 80% in *delaminated* and *intercalated* nanocomposites containing a silicate mass fraction of only 2 % to 6 %. This system does not increase the rate of carbon monoxide generation or the rate of soot produced during the combustion. Just as the nanocomposite structure of the PLS enhances the properties of the polymer, the nanocomposite structure in the char appears to enhance the performance of the char layer. This layer (TEM show in Figure 1) may act as an insulator and a mass transport barrier slowing the escape of the volatile products (mass loss rate) generated as the polymer decomposes.



Figure 1.TEM of a section of the combustion char from the nylon-6 clay-nanocomposite (5%) showing the carbonaceous-silicate (1 nm thick, dark bands) multilayered structure. This layer may act as an insulator and a mass transport barrier, slowing the escape of the volatile products generated as the nylon-6 decomposes.

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